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Theoretical and experimental studies on silica-coated carbon spheres composites

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ABSTRACT

In order to prepare carbon-based photonic crystals, first of all, theoretical modeling calculation was used to predict the bandgap characteristics of silica-coated carbon spheres. Then, silica-coated carbon spheres composites were synthesized using tetraethyl orthosilicate as precursor of silica by a sol–gel method combined with Stöber method. Effect of reaction conditions on surface coating of carbon spheres with silica, including the pH, the amount of precursor and reaction time, was emphasized. The morphology and structure of the composites and the effect coating of carbon spheres with silica were characterized by field-emission scanning electron microscopy, high resolution transmission electron microscopy and Fourier-transform infrared spectrometry. The coating ratio of silica was investigated by thermogravimetry. The results show that pH value played an important role in coating reaction, the dosage of the precursor and reaction time had significant effect on coating layer thickness, that is, coating ratio. Carbon spheres coated with silica had good dispersibility and dispersion stability in water and ethanol, which is preconditions of reactivity of carbon spheres in liquid phase and lays the basis for the application of carbon spheres.

1. Introduction

Photonic crystals are periodic structure optical materials designed on nano-scale by periodical arrangement of more than two materials with different reflective index [1]. Their properties are dependent on their structure. The photonic bandgap is one of the most important properties of photonic crystals. The existence of photonic bandgap make it possible to control the propagation of light as expected, and to find application in optical elements and communication devices with high performance. Han et al. [2,3] adopted a transfer matrix method to find the possibility of fullerene/AlN multilayer films acting as one-dimensional (1D) photonic band gap (PBG) crystals and C_{60} films acting as two dimensional photonic crystal material in ultraviolet (UV), visible and near-infrared region, thus forecasting the potential application of onion-like fullerenes (OLFs) carbon materials in the field of photonic crystals. As C_{60} can be considered as the simplest OLFs, carbon spheres (CSs), with fullerenes-like cage structures composed of fairly concentric graphitic shells, are considered as enlarged onion-like fullerenes. Therefore CSs as building blocks could be used to fabricate photonic crystal. Silica and polymer microspheres are widely used to prepare photonic crystals [4], and self-assembly method by vertical deposition technique is known as a feasible route to fabricate colloidal crystals for its facility, cost-effectiveness, short fabrication period, and crystal layer controllability [5]. CSs, with good chemical, mechanical and thermal stabilities, are promising for materials of photonic crystals. There are many merits using CSs as building blocks in constructing colloidal crystals, including tunable particle size, acid and alkali resistance, and a simple, low-cost and continuous green production approach. For preparing photonic crystals, the building blocks are needed to have good monodispersion and excellent processability in liquid phase. However, as-prepared CSs are of chemically inert surface, and consequently of low dispersion in water and organic solvents, which is the major limitation to the processability of these structures, and greatly hinders the wide application of CSs. Therefore, it is indispensable to modify the surface of CSs to improve the dissolution properties in inorganic and organic solvents, as well

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as the reactivity for subsequent reactions in liquid media. Surface coating is one of the most important methods. From this point of view, silica, a kind of non-toxic, non-polluting material with abundant hydroxyl functional groups, is a very interesting candidate [6].

In this paper, first of all, theoretical modeling and calculation were used to predict the bandgap characteristics of silica-coated CSs; then, CSs–silica core–shell structured material was prepared using tetraethyl orthosilicate (TEOS) as precursor of silica by Stöber method [7]. Effect of reaction conditions on surface coating of CSs with silica, including the pH, the amount of precursor and reaction time, was investigated. The silica-encapsulated CSs composites self-assembled via vertical deposition [8]. The construction of photonic crystals consisting of non-packed CSs via the self-assembly of silica–carbon composite spheres and the subsequent dissolution of the silica is on-going.

2. Experimental

2.1. Materials

CSs were prepared by the pyrolysis of acetylene at atmospheric pressure in a tubular furnace [9]. Tetraethyl orthosilicate (TEOS) (A.R.), anhydrous ethanol, cetyltrimethylammonium bromide (CTAB) (A.R.) and ammonia (25%) were purchased from Tianjin Chemical Corporation (Tianjin, China). Deionized water was prepared with an ion exchange system.

2.2. Coating CSs with silica

CSs (0.5 g) were dispersed in a mixed solution of 8 ml of H_2O and 40 ml of anhydrous ethanol by ultrasonic treatment. After surfactant CTAB (0.086 g) was added into the above solution under ultrasonic irradiation, ammonia was added under vigorous stirring to adjust the pH of the solution. Finally, an appropriate amount of TEOS was added. The reaction mixture was refluxed at 40 °C for a period of time, the products were collected by centrifugation, washed with water and anhydrous ethanol for several times. After drying at 100 °C for 10 h, part of the products was calcinated at 550 °C for 4 h to obtain hollow silica spheres.

2.3. Characterization of materials

The morphology and structure of the sample were characterized by JSM-6700F field emission scanning electron microscope (FESEM) and JEM-2010 high resolution transmission electron microscope (HRTEM) operated at 200 kV. Fourier-transform IR (FTIR) spectra were recorded on a Japan MODEL-8400s FTIR spectrometer using KBr pellet, which were used to further prove the coating of silica on the surface of carbon spheres. The coating ratio was investigated using a Netzsch TG 209F3 thermogravimetric analyzer at a heating rate of 10 °C/min under air atmosphere.

3. Theoretical simulation

Translight software was used to simulate the bandgap characteristics of silica-coated CSs three-dimensional photonic crystals at ultraviolet, visible and near-infrared band (wavelength 200–1000 nm), in which the dielectric constant of silica and CSs was set at 4.5 and 2.8, respectively. The model is shown in Fig. 1. The diameter of CSs was kept constant as 300 nm, the coating ratio of silica (the ratio of coating layer thickness to the radius of CSs) was changed to calculate the lattice parameters, as shown in Table 1. Calculations show that the band gap position appeared in 720–1000 nm. The band gap position moved to infrared regions with the increase of the coating ratio. When the coating ratio exceeded 25%, the band gap moved out of this region, as shown in Fig. 2. On the other hand, it should be noted that the coating ratio had little effect on the width of the band gap, which maintained about 100 nm for different coating ratio. In one word, when the diameter of CSs was set at 300 nm and the dielectric constants of the substrate material and the coating material were defined, the change of coating ratio affected only the position of forbidden band and had little influence on band width.

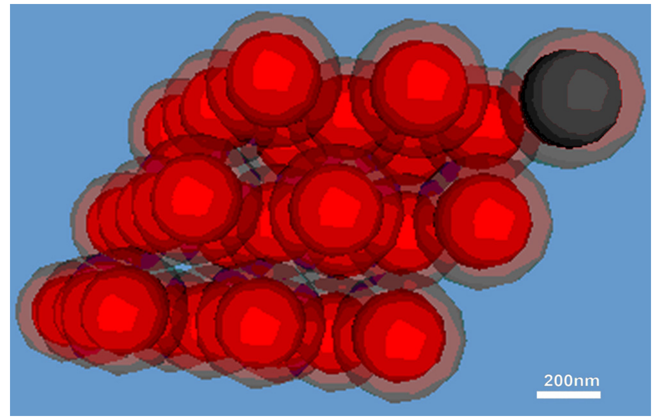

Fig. 1. The model of CSs coated by silica.

Table 1
The lattice constant changed with changing coating ratio (nm).

Coating ratio	0.0%	5.0%	10.0%	15.0%	20.0%	25.0%
Lattice constant	424.26	445.48	466.69	487.90	509.12	530.33

4. Results and discussion

4.1. Influence of solution pH

Theoretical simulation shows that CSs coated by silica existed photonic bandgap in ultraviolet, visible and near-infrared band, which indicates the potential applications of OLFs and CSs in the field of photonic crystals. Based on this research background and the characteristics of carbon materials, this study focused on the surface coating modification of CSs with silica. In recent years, a considerable amount of theoretical and experimental works related to the modification of carbon materials center on carbon nanotubes (CNTs) [10,11]. The reports on the surface modification of

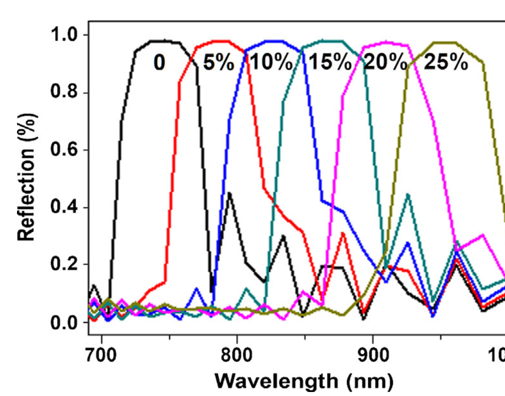

Fig. 2. The relationship of photonic bandgap location and the coating ratio.